

Energy Research and Development Division
FINAL PROJECT REPORT

DIRECT RECYCLING TECHNOLOGY FOR PLUG-IN ELECTRIC VEHICLE LITHIUM-ION BATTERY PACKS

Prepared for: California Energy Commission
Prepared by: Farasis Energy, Inc.

MARCH 2015
CEC-500-2016-016



PREPARED BY:

Primary Author(s):

Phillip Hailey
Keith Kepler

Farasis Energy, Inc.
21363 Cabot Blvd
Hayward, CA 94545
Phone: 510-732-6600
<http://www.farasis.com>

Contract Number: PIR-12-006

Prepared for:

California Energy Commission

Rhetta DeMesa
Contract Manager

Aleecia Gutierrez
Office Manager
Energy Research Office

Laurie ten Hope
Deputy Director
ENERGY RESEARCH AND DEVELOPMENT DIVISION

Robert P. Oglesby
Executive Director

DISCLAIMER

This report was prepared as the result of work sponsored by the California Energy Commission. It does not necessarily represent the views of the Energy Commission, its employees or the State of California. The Energy Commission, the State of California, its employees, contractors and subcontractors make no warranty, express or implied, and assume no legal liability for the information in this report; nor does any party represent that the uses of this information will not infringe upon privately owned rights. This report has not been approved or disapproved by the California Energy Commission nor has the California Energy Commission passed upon the accuracy or adequacy of the information in this report.

ACKNOWLEDGEMENTS

This work was supported by the California Energy Commission's Public Interest Energy Research program under agreement number PIR-12-006.

Farasis Energy, Inc. would like to thank the California Energy Commission and its staff for supporting this project.

The research team would like to give special thanks to key partner Lawrence Berkeley National Laboratory for providing support in materials characterization. They specifically give thanks to Lydia Terborg for performing XRD characterization and analysis and to Robert Kostecki for technical guidance throughout the project.

PREFACE

The California Energy Commission Energy Research and Development Division supports public interest energy research and development that will help improve the quality of life in California by bringing environmentally safe, affordable, and reliable energy services and products to the marketplace.

The Energy Research and Development Division conducts public interest research, development, and demonstration (RD&D) projects to benefit California.

The Energy Research and Development Division strives to conduct the most promising public interest energy research by partnering with RD&D entities, including individuals, businesses, utilities, and public or private research institutions.

Energy Research and Development Division funding efforts are focused on the following RD&D program areas:

- Buildings End-Use Energy Efficiency
- Energy Innovations Small Grants
- Energy-Related Environmental Research
- Energy Systems Integration
- Environmentally Preferred Advanced Generation
- Industrial/Agricultural/Water End-Use Energy Efficiency
- Renewable Energy Technologies
- Transportation

Direct Recycling Technology for Plug-in Electric Vehicle Lithium-ion Battery Packs is the final report for the Direct Recycling Technology for California's PEV Li-ion Battery Packs project (contract number PIR-12-006) conducted by Farasis Energy, Inc. The information from this project contributes to Energy Research and Development Division's Transportation Program.

For more information about the Energy Research and Development Division, please visit the Energy Commission's website at www.energy.ca.gov/research/ or contact the Energy Commission at 916-327-1551.

ABSTRACT

The eventual disposal of used lithium-ion battery systems from aging electric vehicles has been recognized as a major issue that needs to be addressed. No infrastructure currently exists for the efficient disposal or recycling of these large and hazardous battery systems, and traditional methods of recycling only allow for the recovery of battery metals in a relatively low-value form.

In this project, the research team investigated the development of a new direct recycling process for lithium-ion batteries. During this process, a used battery cell's high-value cathode and anode active powders (for example, lithium nickel manganese cobalt oxide and graphite) are recovered whole, 2) separated from each other and from the other recoverable materials such as copper and aluminum metal, and 3) returned to their original state for direct reintroduction into new lithium-ion battery cells. The direct recycling process allows for the recovery of most of the cell's lithium content and graphite, both of which would otherwise be unclaimed in the traditional recycling process because of their low cost and low demand for use in other applications.

Direct recycling is currently the only recycling approach in which a large portion of the materials recovered from spent lithium-ion cells would directly reenter the lithium-ion battery market, making the process more environmentally friendly than traditional recycling processes. The research team's investigation proved successful with the achievement of a complete life cycle demonstration of a recycled lithium-ion battery. These results reveal that the direct recycling process is a promising technology that could provide lower-cost materials to battery manufacturers and in turn drive the total electric vehicle battery system cost down so that electric vehicles can be less costly in the near future.

Keywords: direct recycling, battery recycling, recycling technology, lithium-ion cell, li-ion cell, li-ion battery, li-ion batteries, electric vehicle, cathode, anode, recycled battery material

Please use the following citation for this report:

Hailey, Phillip; Keith Kepler. (Farasis Energy, Inc.). 2016. *Direct Recycling Technology for Plug-in Electric Vehicle Lithium-ion Battery Packs*. California Energy Commission.
Publication number: CEC-500-2016-016.

TABLE OF CONTENTS

| | |
|-----------------------------------------------------------------------------|-----|
| Acknowledgements | i |
| PREFACE | ii |
| ABSTRACT | iii |
| TABLE OF CONTENTS..... | iv |
| LIST OF FIGURES | v |
| LIST OF TABLES | v |
| EXECUTIVE SUMMARY | 1 |
| Introduction | 1 |
| Project Purpose | 1 |
| Project Results..... | 2 |
| Project Benefits | 2 |
| CHAPTER 1: Introduction..... | 3 |
| 1.1 Need for Li-ion Battery Recycling Infrastructure | 3 |
| 1.2 Justification for Recycling High-Value Li-ion Battery Materials..... | 4 |
| 1.3 Direct Recycling of Li-ion Batteries | 6 |
| 1.4 Feasibility of Reusing Li-ion Battery Materials..... | 6 |
| 1.5 Project Goals | 7 |
| CHAPTER 2: Direct Recycling Process | 8 |
| 2.1 Process Outline | 8 |
| 2.2 Li-ion Battery / Cell Disassembly..... | 9 |
| 2.3 Separation of Active Materials | 10 |
| 2.4 Purification of Active Materials | 11 |
| 2.5 Regeneration of Active Materials | 11 |
| CHAPTER 3: Results & Discussion..... | 14 |
| 3.1 Materials Characterization..... | 14 |
| 3.1.1 X-ray Diffraction (XRD)..... | 14 |
| 3.1.2 Thermogravimetric Analysis (TGA)..... | 15 |

| | | |
|--------------------------------------------------------|---------------------------------------------------------|-----------|
| 3.1.3 | Scanning Electron Microscopy (SEM) | 15 |
| 3.2 | Test Methods..... | 16 |
| 3.3 | Life-Cycle Demonstration of Recycled Li-ion Cells | 18 |
| CHAPTER 4: Conclusions and Recommendations..... | | 22 |
| 4.1 | Conclusions..... | 22 |
| 4.2 | Recommendations..... | 22 |
| 4.3 | Benefits to California | 22 |
| GLOSSARY | | 23 |

LIST OF FIGURES

| | | |
|------------|--------------------------------------------------------------------------------|----|
| Figure 1: | Projected Electric Vehicle Adoption Rates in California..... | 3 |
| Figure 2: | Flow Diagram for Direct Recycling of Lithium-ion Batteries | 8 |
| Figure 3: | Harvesting Electrode Material from 10Ah Li-ion Cells | 10 |
| Figure 4: | Separation of Anode and Cathode Powders | 10 |
| Figure 5: | Optimization of Lithium Content in Recycled Cathode Materials..... | 13 |
| Figure 6: | X-ray Diffraction Spectra for Treated NMC Cathode Materials..... | 14 |
| Figure 7: | Electron Microscope (SEM) Images of Pristine and Recycled Anode Particles..... | 15 |
| Figure 8: | Voltage Curves of Pristine and Recycled Anode Materials..... | 16 |
| Figure 9: | Voltage Curves of Pristine and Recycled Cathode Materials..... | 18 |
| Figure 10: | 10Ah and 25Ah Lithium-ion Pouch Cells Manufactured by Farasis | 19 |
| Figure 11: | Cycle Performance Testing of Pouch Cells Used for Recycling Process..... | 20 |
| Figure 12: | Cycle Performance of Cells Made from Direct Recycled Materials..... | 21 |

LIST OF TABLES

| | | |
|----------|--------------------------------------------------------------------------------------|---|
| Table 1: | Comparison of Existing Recycling Processes to Proposed Direct Recycling Process..... | 5 |
|----------|--------------------------------------------------------------------------------------|---|

EXECUTIVE SUMMARY

Introduction

One major issue that electric vehicle (EV) manufacturers must consider as the electric vehicles on the road age and wear down is the safe and efficient disposal of spent lithium-ion (Li-ion) batteries. There is currently no established system for disposing of or recycling these large, environmentally hazardous Li-ion battery systems. The traditional recycling methods that are currently being used cannot support a growing EV market as they are both inefficient and uneconomical, only allowing recovery of the battery's metal components in a relatively low-value form.

Unless a new recycling approach tailored to the Li-ion battery system is developed as the EV market grows, California and other states will be faced with the difficult choice to either 1) accept a massive increase in the amount of hazardous material that must be processed and taken in by their landfills, or 2) charge fees related to the purchase or use of EVs that can be used to support a conventional recycling/disposal infrastructure for spent EV battery packs.

A research team from Farasis Energy Inc., a Li-ion battery manufacturer with headquarters in Hayward, California, has recognized that a market shift to EVs could have a disruptive impact on the battery recycling industry by increasing the number of spent battery systems in the near future. This shift represents a unique opportunity for both manufacturers of Li-ion batteries and battery recycling companies to make advances in battery recycling technology, particularly if they work together to develop the critical technology that will be used to recycle the cells.

The research team has been conducting ongoing research to identify and evaluate solutions to some of the technical issues associated with a *direct recycling* approach, which is modeled after the highly successful recycling approach used by the lead-acid battery industry. Compared to existing Li-ion battery recycling approaches, direct recycling can be self-sustaining and would be more environmentally friendly. Materials from spent Li-ion cells would be recovered in a condition suitable for direct re-entry into the Li-ion battery market, providing a lower-cost alternative to battery manufacturers and serving to drive down the cost of new Li-ion cells.

Project Purpose

The goal of the project was to develop and demonstrate the technical feasibility of a direct recycling technology suitable for handling the large number of plug-in electric vehicle (PEV) Li-ion battery packs that will enter the waste stream over the coming decades.

The research team collaborated with the University of California's Lawrence Berkeley National Laboratory to develop, optimize, and scale up the key steps of the direct recycling process by comparing the lab-scale process to the industrial scale process. They analyzed the impact of each step of the direct recycling process on the Li-ion battery material properties to improve processing conditions and identified potential process/material incompatibilities. The team took into account many of the variables associated with the incoming Li-ion battery waste stream, and demonstrated that the cost structure could lead to a self-sustaining recycling industry.

Project Results

The research team successfully demonstrated a complete lab-scale life cycle of the direct recycling technology. Lithium-ion cells that had been charged and discharged through more than 2,000 cycles were disassembled, and their electrode materials were ground, separated, purified, regenerated, and finally formed into new electrodes and cells. The research team then subjected these cells to life cycle testing, and after 250 cycles, capacity retention of cells using 100 percent recycled active materials was still within 5 percent that of control cells made using new materials.

Project Benefits

The progress made over the course of this project could lay the foundation for a viable recycling technology that can help determine how Li-ion batteries are recycled in the future. As a global leader in advancing electric vehicle technology and the mainstream adoption of EVs, California stands to benefit directly from investing in and establishing a direct recycling industry for Li-ion batteries. Materials salvaged from spent batteries through direct recycling will be sold back to battery manufacturers and used to manufacture new cells. This sustainable, environmentally system will provide a dependable revenue stream to support the battery recycling business. Furthermore, since most of the cost of new Li-ion battery active materials is associated with their synthesis rather than their metal content, the availability of these lower-cost materials will help to bring down the cost of Li-ion cell manufacturing and ultimately drive the total EV battery system cost down in the near future.

CHAPTER 1:

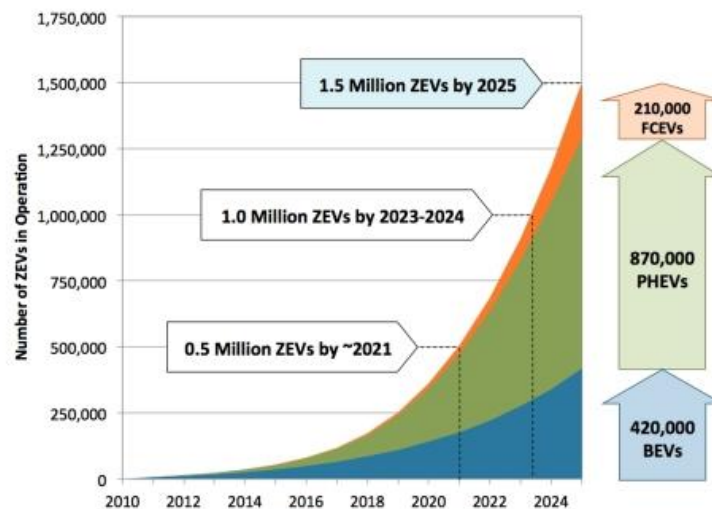
Introduction

1.1 Need for Li-ion Battery Recycling Infrastructure

Despite major technical progress in the development of electric vehicles (EVs), their high cost is a significant barrier preventing rapid growth of the EV market. Furthermore, disposal of spent lithium ion (Li-ion) battery systems powering this new generation of vehicle has been recognized as a major issue that will need to be addressed as the market grows and EVs now on the road begin to fail.

No infrastructure currently exists for disposing of or recycling these very large, hazardous Li-ion battery systems. Even though Li-ion batteries are widely used in consumer electronics applications, they are widely dispersed, difficult to collect and have little value if recycled, so no recycling infrastructure has developed to handle them. Furthermore, existing methods of recycling Li-ion batteries rely on the recovery of only a very small portion of the battery, typically cobalt metal, which has sufficient value to justify the effort. However, cobalt is used less and less in newer Li-ion systems used for plug-in electric vehicles (PEVs), and the processing methods used, such as smelting or digestion, result in the destruction or burn off of all of the high value active materials, including lithium.

Figure 1: Projected Electric Vehicle Adoption Rates in California



Source: Marc Melaina and Michael Helwig¹

¹ Melaina, Marc, Michael Helwig (National Renewable Energy Laboratory) 2014. California Statewide Plug-in Electric Vehicle Infrastructure Assessment. California Energy Commission. Publication number: CEC-600-2014-003.

Figure 1 shows an estimate of the projected EV adoption growth rates in California through 2025. Unless a new recycling approach is developed specifically to handle the large Li-ion battery systems that will be generated as the EV market grows, California and other states will face the choice of either accepting a massive increase in the amount of hazardous material that must be processed and taken in by their landfills, or face the necessity of charging fees related to the purchase or use of EVs that can be used to support a conventional recycling/disposal infrastructure for EV battery packs. Neither option is desirable, since both could significantly increase the purchase cost of EVs for the consumer and hinder the shift away from combustion engines that are desired to address a range of major environmental and economic concerns.

Funding for this effort is critical now, since it is highly likely that the first to establish a viable recycling technology will determine how batteries are recycled in the future. California stands to benefit from both the direct recycling technology being proposed, and from becoming the leader in establishing a Li-ion battery recycling industry.

1.2 Justification for Recycling High-Value Li-ion Battery Materials

Currently, Li-ion batteries based on a LiCoO_2 (Lithium Cobalt Oxide, LCO) cathode and graphitic carbon anode chemistry represent about 60 percent of the Li-ion battery market. At \$35 to \$45 per kilogram, the LCO active cathode material is an expensive component. If recycled using a traditional method, it is either melted (smelting) or dissolved (hydrothermal), but not recovered as the active LiCoO_2 phase, suitable for reuse in a Li-ion cell. The resulting alloy that forms from such processing requires extensive purification to produce cobalt suitable for its various market segments. Furthermore, only a fraction of recovered cobalt undergoes processing to become battery material again. Therefore, an economic and environmental mismatch exists between current recycling practices and current Li-ion battery technology, leading to a lost opportunity to achieve materials price stabilization due to the movement of recovered material from batteries to other products. The highly processed graphitic carbon anode active materials (\$10 to \$25 per kilogram) are also generally not recovered by conventional recycling processes and, along with lithium, are lost during smelting processes focused on recovering valuable metals.

To further diminish the economic rationale for conventional smelting or hydrothermal recycling approaches, the remaining 40 percent of the Li-ion battery market is based on cobalt-dilute and cobalt-free Li-ion chemistries (For example, LiMn_2O_4 , LiNiCoMnO_2 , and LiFePO_4) which have almost no value in terms of metal content, but typically cost greater than \$20 per kilogram. These low-cobalt chemistries are rapidly displacing LCO as the dominant cathode material in new generations of battery applications. As a result, there will be little economic justification for recycling these batteries and no contribution to price stability.

For environmental reasons, Li-ion battery recycling would likely have to be supported by a user fee, adding to the cost of Li-ion batteries and slowing the introduction of price sensitive battery applications such as EVs. To address this dilemma, a technical strategy to reclaim whole materials (specifically, cathode and anode active materials) can realize value, even from cells utilizing active materials that are completely free of valuable metals such as cobalt. Table 1

compares outcomes from conventional smelting and hydrometallurgy with the direct recycling approach for LCO or LiFePO₄ based batteries. On one hand, high temperatures or aggressive chemicals can disintegrate the anode and cathode active materials, and on the other, a direct recycling approach efficiently recovers them in-whole.

Table 1: Comparison of Existing Recycling Processes to Proposed Direct Recycling Process

| Battery Component | Smelting Outcome | Hydrometallurgy Outcome | Direct Recycling Process Outcome |
|--------------------------|----------------------------|--------------------------------|-----------------------------------------|
| Lithium Iron Phosphate | N/A | Impure Iron oxide | Lithium Iron Phosphate |
| Lithium Cobalt Oxide | Impure Cobalt alloy | Impure Cobalt oxide | Lithium Cobalt Oxide |
| Carbon/graphite | Destroyed | Waste product | Carbon/Graphite Product |
| Electrolyte Compounds | Destroyed | Destroyed | Electrolyte Product |
| Copper | Impure Cobalt/Copper alloy | Dissolved, Copper oxide | Solid recovery |
| Aluminum | Slag body | Dissolved | Solid recovery |
| Steel | Cobalt/Copper/Iron alloy | Dissolved, Iron oxide | Solid recovery |

Source: Farasis Energy, Inc

An ideal recycling solution for large PEV Li-ion battery packs would enable recycling of the majority of the mass/volume of the battery pack, would recover the materials in a form that could be reused in new battery systems, and would be financially supported by the sale of the recovered materials, without additional fees or government subsidies. The lead-acid battery industry provides a good model for such a system, where greater than 97 percent of the lead used to make new lead-acid batteries comes from recycled lead-acid batteries. The system simultaneously removes hazardous lead from the disposal stream and minimizes the need for any additional mining for new sources of lead, which itself is quite hazardous to the environment.

In addition to these benefits, the business of recycling lead-acid batteries can be very profitable for companies such as RSR Technologies and their parent company ECO-BAT, which has revenue exceeding \$1 billion per year worldwide. The existence of this recycling infrastructure has led lead-acid batteries to become one of the cheapest battery systems in terms of dollar per watt-hour currently available on the market. This is one of the major reasons other battery technologies have had such difficulty displacing lead-acid batteries despite major performance advantages. As such an infrastructure is built to support Li-ion battery direct recycling, similar cost advantages will be realized for the battery technology.

1.3 Direct Recycling of Li-ion Batteries

Direct recycling refers to a novel recycling approach for Li-ion batteries, in which the high value anode and cathode active powders (for example, lithium nickel manganese cobalt oxide (NMC) and graphite) are recovered in whole from spent cells, separated from each other and from the other recoverable materials such as copper and aluminum metal, and then regenerated to their original state for direct reintroduction into new Li-ion cells. This approach to recycling establishes a closed cycle in which the high value materials are reintroduced into new batteries, while other recoverable components (primarily metals) would flow into existing recycling markets; the waste stream comprises only the small volume of polymer components such as the separator and binder.

Farasis has previously worked with RSR and Onto Technologies to develop various aspects of the direct recycling process, primarily with a focus on LCO/graphite chemistry because of the more readily available source of spent LCO cells. Based on the promising results of this foundational work, the scope of cathode chemistry for this project is expanded to the NMC class of materials, which is becoming more prevalent in large EV systems.

1.4 Feasibility of Reusing Li-ion Battery Materials

Li-ion cells generally contain two active materials: the anode, usually graphite, and the cathode, which is a type of lithium metal oxide (for example, LCO or NMC). When used to build a Li-ion cell the active cathode material initially contains 100 percent of the lithium in the cell, and the graphite anode contains no lithium. As a Li-ion cell is charged, some of the lithium moves from the cathode to the anode, so that when the cell is fully charged, the cathode is partially de-lithiated and the anode is partially lithiated; in this state, neither material could be reused to make new Li-ion cells. In contrast, if the cell is fully discharged, then theoretically the cathode and anode would be in their originally assembled state, and if recovered, these materials could be used again to make a new Li-ion cell.

However, any cell that has been cycled even once has already permanently lost some of its active lithium to a number of unavoidable side reactions. Thus, it is not possible to simply discharge an old cell, open it, and recover fully lithiated cathode and fully de-lithiated anode active materials for use in a new Li-ion cell. Some of the lithium has been depleted from the cathode and needs to be added back to the recovered cathode material to return it to its original composition. Likewise, some of the lithium is trapped in the recovered anode material, and must be removed to return the anode back to a stable, pure graphite material that can be handled safely in a high-volume manufacturing environment.

While variable between different Li-ion cell chemistries, much of the capacity loss associated with an aged Li-ion cell is the result of impedance increases related to side reactions or electrolyte depletion, and not from damage to the active material structure. For some Li-ion chemistries, the cycled active anode and cathode materials are almost fully functional, retaining their original structure, even after the cell performance has degraded to the point that the cell must be replaced. Thus, recycling intact active materials from Li-ion cells is technically feasible

and represents the most practical and efficient way to establish a recycling chain for the Li-ion market.

1.5 Project Goals

The specific objectives of the project were outlined as follows:

- Develop processes and characterize materials to demonstrate that the proposed direct recycling approach can produce Li-ion battery active materials similar in performance to that of newly synthesized battery materials that will be suitable for reuse in new Li-ion batteries for EV applications.
- Optimize and demonstrate that the recycling process steps have the potential to recover and regenerate active materials and inactive materials with high yield.
- Demonstrate that the approach is suitable for the dominant Li-ion battery waste streams expected for PEV systems in California and the feasibility of its broad use for a range of Li-ion battery chemistries with further optimization.
- Demonstrate one life cycle of a Li-ion cell at the lab scale.

CHAPTER 2:

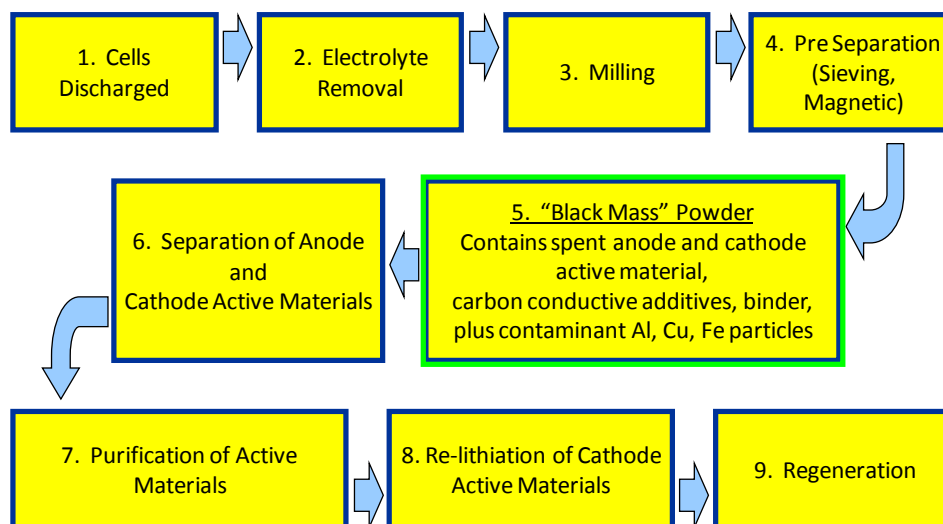
Direct Recycling Process

2.1 Process Outline

The direct recycling process encompasses a closed cycle in which the high value materials, such as the active cathode material particles (for example, LCO and NMC) and anode particles (graphite) are recovered from old Li-ion batteries, regenerated, and used to make new batteries. Other components such as aluminum and copper metal would flow into existing recycling markets, with the loss of only the small volume of polymer components such as the separator and binder.

Farasis has been working to develop various aspects of the direct recycling process for several years, primarily with a focus on LCO/graphite chemistry due to the more readily available source of spent cells with this chemistry. Figure 2 shows a general flow chart for the proposed direct recycling process.

Figure 2: Flow Diagram for Direct Recycling of Lithium-ion Batteries



Source: Farasis Energy, Inc

Used battery packs would be taken from service and collected, discharged, and dismantled. The cells are shredded using industrial machinery. After cell shredding the material may be treated to remove residual electrolyte for potential reuse; this step would also stabilize the cell chemistry by removing a source of hydrofluoric acid, which can damage the Li-ion active materials as the materials are handled in air and water during subsequent processing. After electrolyte leaching, the material is screened to remove casings, separators, and plastics from the micron-sized active materials. These larger materials would then flow into the existing recycling industry, leaving primarily a powdery mixture of active anode and cathode particles, with some binder and metal contaminant materials.

In this state, the recovered active materials are not immediately ready for use in new Li-ion cells for a number of reasons. The recovered cathode material will be missing some lithium due to natural loss during the cell formation process and during cycling, and the graphite anode material will likely contain some lithium and surface species generated during the formation and cycling processes. Any contaminants present will also make the active materials unusable in most Li-ion battery cell designs.

Because of this, the next steps in the process, while technically challenging, are critical to the success of the direct recycling approach. They involve the separation of the cathode and anode active materials from each other; purification of these materials, including removal of metal contaminants; replenishing the lithium content in the cathode material; and finally, regeneration of the anode and cathode materials, during which the surface structure of the materials is returned to a pristine state.

Farasis has proposed and developed a number of proprietary approaches to achieving these final steps, and it was a major goal of this project to optimize these processes and demonstrate their efficacy in producing high-quality recycled materials suitable for use in new Li-ion cells.

2.2 Li-ion Battery / Cell Disassembly

At an industrial scale, entire cells are shredded by a milling machine, and the resulting material could be subjected to a leaching step which removes the electrolyte for potential reuse. This step also stabilizes the cell chemistry by removing a source of hydrofluoric acid, which can damage the Li-ion active materials as the materials are handled in air and water during subsequent processing. After leaching, the material is screened to remove casings, grids, separators, and plastics from the micron sized active materials. This detritus is sent to the existing metals recycling industry leaving only a mixture of active anode and cathode particles with some binder and metal contaminants.

At the lab scale, for reasons of safety and practicality, individual cells were disassembled by hand after being either fully discharged, or discharged to a desired state of charge for experiments to mimic real life SOC variability of incoming cells. The anode and cathode electrodes were thus separated from the aluminum laminate pouch material, the tabs, and the separator. The electrodes were then soaked in a solvent and rinsed to remove electrolyte, and thoroughly dried prior to being ground together into fine powders creating a black mass similar in composition to what would be produced from an industrial scale process through Step 4 shown in Figure 2. A key aspect of the development approach is the co-milling of the anode and cathode electrodes since perfect separation of the anode and cathode electrodes from each other during cell disassembly to enable separate processing paths is not very practical for an industrial scale process.

Figure 3: Harvesting Electrode Material from 10Ah Li-ion Cells



Photo Credit: Farasis Energy, Inc.

2.3 Separation of Active Materials

One of the major challenges to the successful implementation of a direct recycling process lies in being able to effectively separate the anode and cathode material fractions once the cells have been milled to a fine powder. Farasis has developed a method of separation based on the relative density difference between the anode material (graphite), and the much denser transition metal oxide cathode materials. By slurrying the black mass in a solution of dense liquid – the density of which lies between those of the anode and cathode—and allowing the slurry to equilibrate, over time the cathode particles will sink to the bottom of the solution, and the anode particles will rise to the top of the solution (see Figure 4). This process is easily scalable, and also can be accelerated by centrifugation.

Figure 4: Separation of Anode and Cathode Powders



Photo Credit: Farasis Energy, Inc.

Historically, such dense liquids have been used in the mining industry to separate valuable ores from less valuable minerals. Until recently, the liquid density necessary (about 2.2 to 3.5 g/cc) for these separations has been achieved by only a handful of organic compounds, such as bromoform, methylene iodide, and tetrabromoethane, all of which have considerable safety concerns which can be mitigated through sound engineering practices.

While initial laboratory experiments made use of bromoform, the project focused on a more environmentally-friendly process using a relatively new class of aqueous (water-based) dense liquids. These non-toxic alternatives present unique challenges and are generally much more viscous than the organic heavy liquids, but are also fully recoverable and recyclable, and fit well with the project's vision for a closed-loop, green technology. Separation experiments using the aqueous dense liquids were successfully scaled from 10mL to 500mL, with separation yields in excess of 90 percent. Separation efficiency and yield could be improved further by iterative processing using either batch or continuous methods.

2.4 Purification of Active Materials

After the anode and cathode materials have been separated out from a mixed powder, they will invariably need to be purified to be useable as active materials in a new cell. There will always be some degree of contamination in the anode and cathode fractions that will need to be removed, as will any aluminum and copper metal foil fragments from the electrodes that may be present due to the milling process.

To ensure proper electrochemical operation in a battery cell using recycled active materials, the project developed and refined techniques to achieve high levels of purity in the separated anode and cathode powders. The anode fraction is subject to a controlled mild acid (low pH) treatment to remove any mixed cathode particles; a treatment with an alkaline solution (high pH) removes any aluminum or copper present.

Similarly, the cathode is treated with base, and a high temperature firing step removes any residual anode particles that may be present. These purification steps were optimized to achieve greater than 99 percent purity in the final active materials. The treatment solutions can also be fully recovered and reused, and the aluminum and copper could be precipitated and recovered if desired.

The process yields for the purification of anode and cathode powders were greater than 99 percent, and the processes are easily scalable. The active materials (NMC and graphite) were studied before and after purification treatment and found to be chemically stable to the optimized conditions.

2.5 Regeneration of Active Materials

The final step in the direct recycling process is the regeneration of anode and cathode materials. The pristine active cathode materials used in a lithium-ion cell are typically lithium-metal-oxides, such as LCO or NMC. Pristine anode material is usually either a natural or synthetic graphite, and contains no lithium. As the cell is cycled, the lithium shuttles back and forth between the materials, and over many cycles some of this lithium becomes trapped in the

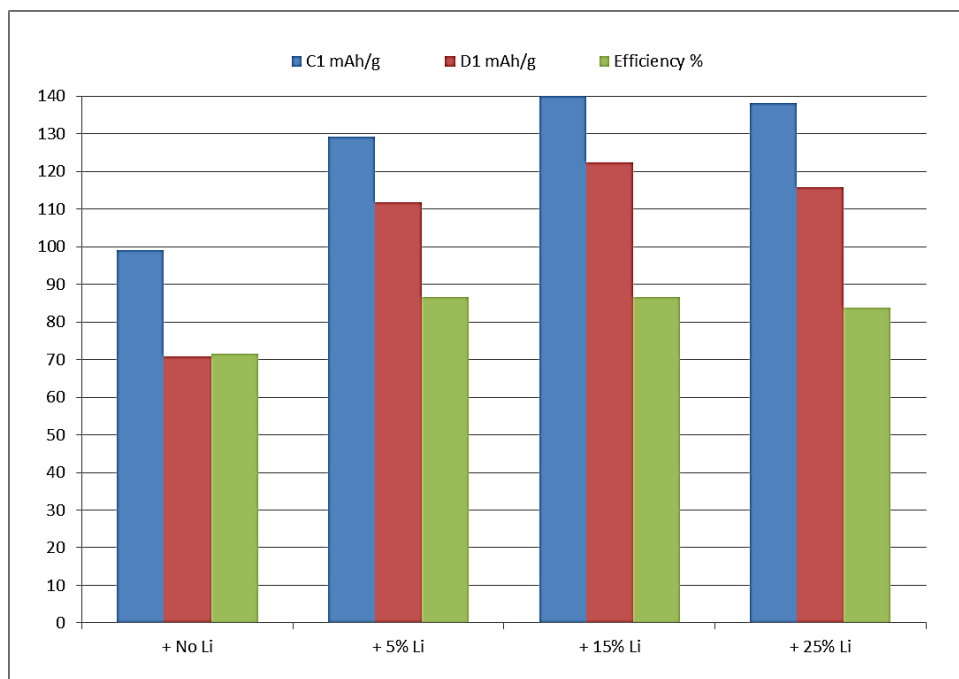
anode, or is consumed in unavoidable side reactions. Thus it is not possible to simply discharge an old cell, open it and recover fully lithiated cathode and fully delithiated anode active materials for use in a new Li-ion cell. There will always be the necessity of adding lithium to the cathode material recovered from a Li-ion cell to return it to the pristine material composition, and removing lithium from an anode recovered from a Li-ion cell to make the stable delithiated form that can be handled in a high-volume manufacturing environment.

Farasis has developed processing techniques that effectively transform the recycled anode and cathode particles into reusable materials that perform nearly as well as pristine materials. Simple treatment in a solvent solution, followed by baking in a furnace, is effective in removing lithium from the anode powder. Process yield was highly dependent on temperature, and when optimized was in excess of 94 percent. Depending on temperature, baking can also remove polymer binder and/or conductive carbon additives that may be present in the anode powder, which may account for a portion of the observed yield loss.

The lithium content of the cathode material must also be adjusted to the proper amount. It is first desirable to obtain an accurate measure of the amount of lithium present in the reclaimed cathode material. In practice, since the material will originate from various cells with different histories, an intermediate equilibration step may be necessary to partially lithiate the material to an average, but not necessarily complete value. Chemical analysis can be performed to determine the average lithium content. Lithium carbonate or lithium hydroxide is then reacted with the recycled cathode material in a high temperature furnace for an extended period of time, after which any unreacted lithium component must be removed through a dissolution and filtration step. Once thoroughly dried, the final recycled cathode material closely resembles the pristine starting material.

Figure 5 shows the effect of varying the amount of lithium addition during the cathode regeneration process collected in one experiment during this project. Coin cells were made and tested from recycled cathode samples with 0, 5, 15, and 25 percent lithium added. Before lithium addition, the recycled material had a low capacity of 99 mAh/g, and very poor first cycle efficiency. The capacity and efficiency reached a maximum at 15 percent added lithium, after which further lithium addition proved slightly deleterious to the material properties.

Figure 5: Optimization of Lithium Content in Recycled Cathode Materials



Source: Farasis Energy, Inc.

Regeneration of the recycled cathode material is similar to the final step in pristine cathode material synthesis, so it is an easily scaled and highly efficient process.

CHAPTER 3:

Results & Discussion

3.1 Materials Characterization

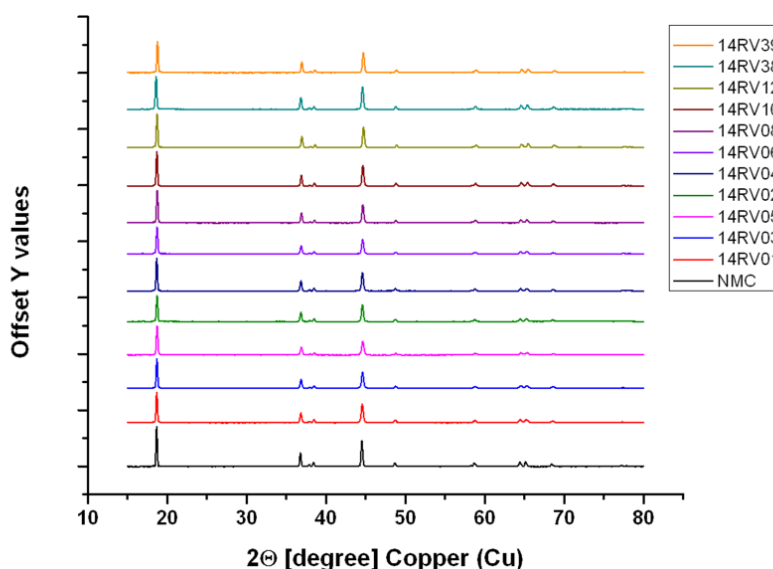
To determine the efficacy of each step in the direct recycling process, a variety of characterization techniques were used.

3.1.1 X-ray Diffraction (XRD)

X-ray diffraction is an analysis technique that can be applied to a powdered material sample to determine its crystallographic properties. The cathode materials used in lithium-ion cells are crystalline, and yield specific spectra, or set of peaks, when exposed to this X-ray technique; comparing the spectrum of a recycled cathode powder to its pristine counterpart can help determine whether impurities are present in the recycled material or if it has changed to a less desirable structure.

XRD analyses were performed by staff at LBNL to compare the structure and purity of cycled, and recycled, anode and cathode materials to their pristine counterparts. XRD spectra were acquired for samples of cathode material harvested from new cells, and from cycled cells, and compared to those obtained from pristine cathode powders (see Figure 6). In all cases the XRD patterns were found to agree with the starting material, suggesting that no serious damage was done to the structure of the cathode material throughout the lifetime of a lithium ion cell.

Figure 6: X-ray Diffraction Spectra for Treated NMC Cathode Materials



Source: Lawrence Berkeley National Laboratory (LBNL)

Samples of recycled anode and cathode were also analyzed after going through the entire direct recycling process, and compared to the pristine materials. Again, the XRD patterns did not

differ significantly from the pristine materials, suggesting that the optimized process steps were not harming the materials at a structural level.

3.1.2 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) is a technique used to measure weight loss of a sample as it is heated in a small furnace. TGA was performed at Farasis to determine the efficacy of the separation process. Anode material (graphite) and conductive carbon will decompose at a much lower temperature than cathode material, so analyzing the weight of a sample as it is heated can reveal how much anode remained in the cathode fraction after separation, and vice-versa.

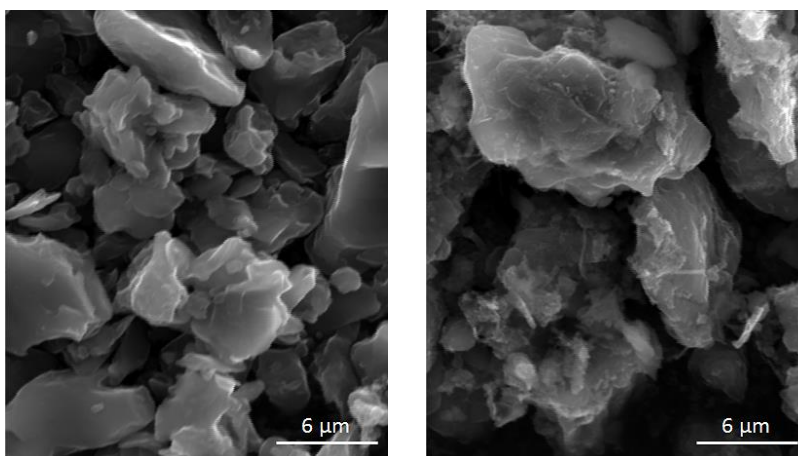
Use of the TGA technique aided optimization of the separation process to maximize the degree of separation. TGA was also used to determine the purity of the anode and cathode materials after the purification steps, and verify that greater than 99 percent purity was achieved in the final recycled material.

3.1.3 Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) aided in the analysis of recycled anode and cathode particle morphology. The SEM technique allows visualization of particle morphology, and the size and shape of the recycled materials were compared to their pristine counterparts. Images of the anode and cathode particles were obtained at various stages throughout the life of a cell, and throughout the direct recycling process.

For the most part, the recycled graphite anode particles appeared to be of the same size and morphology as the pristine graphite particles, even after having been processed through all of the direct recycling steps (see Figure 7).

Figure 7: Electron Microscope (SEM) Images of Pristine and Recycled Anode Particles



Source: Farasis Energy, Inc.

The NMC metal oxide cathode particles, on the other hand, appeared much more fragile. SEM images show that during the initial fabrication of a cathode electrode, the pristine NMC particles undergo compression and are fractured to a much greater degree than previously suspected. Thus, the recycled cathode material is composed of a larger fraction of smaller pieces

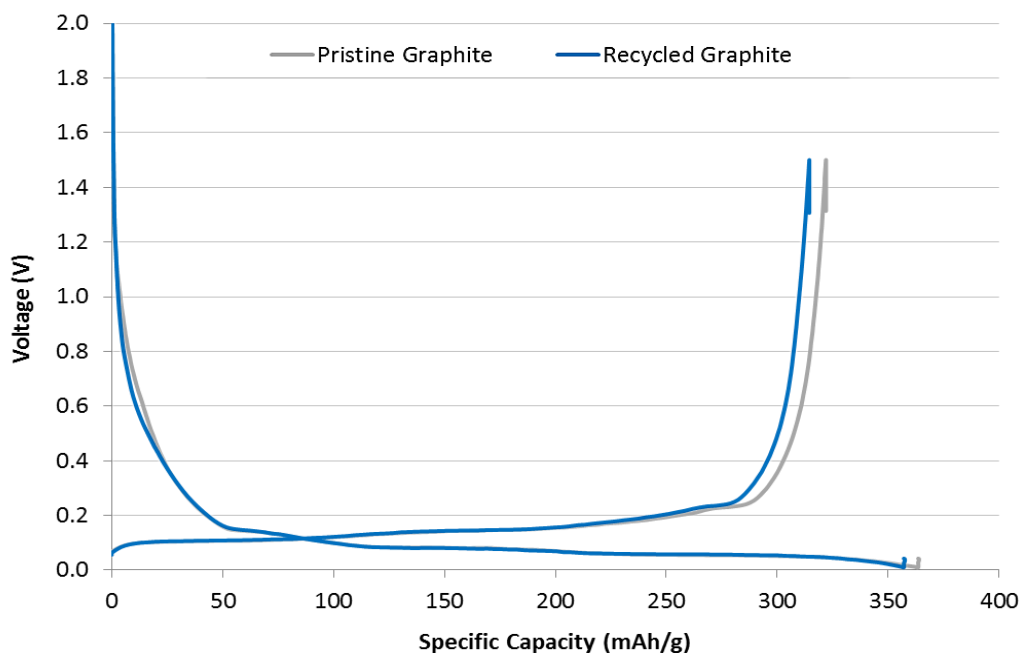
of cathode particles, compared to the pristine material. Whether this affects the long term performance of the recycled cathode in a new cell will need further investigation.

3.2 Test Methods

At each step in the direct recycling process, Farasis carried out extensive electrochemical characterization of the recycled anode and cathode materials to evaluate how well the materials would perform in a new cell compared to pristine materials. New electrodes were formed out of each material sample of interest; the material powders were mixed with conductive additives, polymer binder, and solvent to make a paint-like slurry. The slurry was then cast onto a thin foil (copper for the anode, aluminum for the cathode), and dried in a vacuum oven.

Discs were punched out of either the anode or cathode electrodes, and assembled into lithium button-type coin cells, using a disc of lithium metal as the opposite electrode. Such *half-cells* allow evaluation of the anode or cathode performance independently; the cells can be cycled (charged and discharged) just like a normal full cell, and the electrochemical profile of the recycled anode or cathode can be compared to that of the like pristine material.

Figure 8: Voltage Curves of Pristine and Recycled Anode Materials



Source: Farasis Energy, Inc.

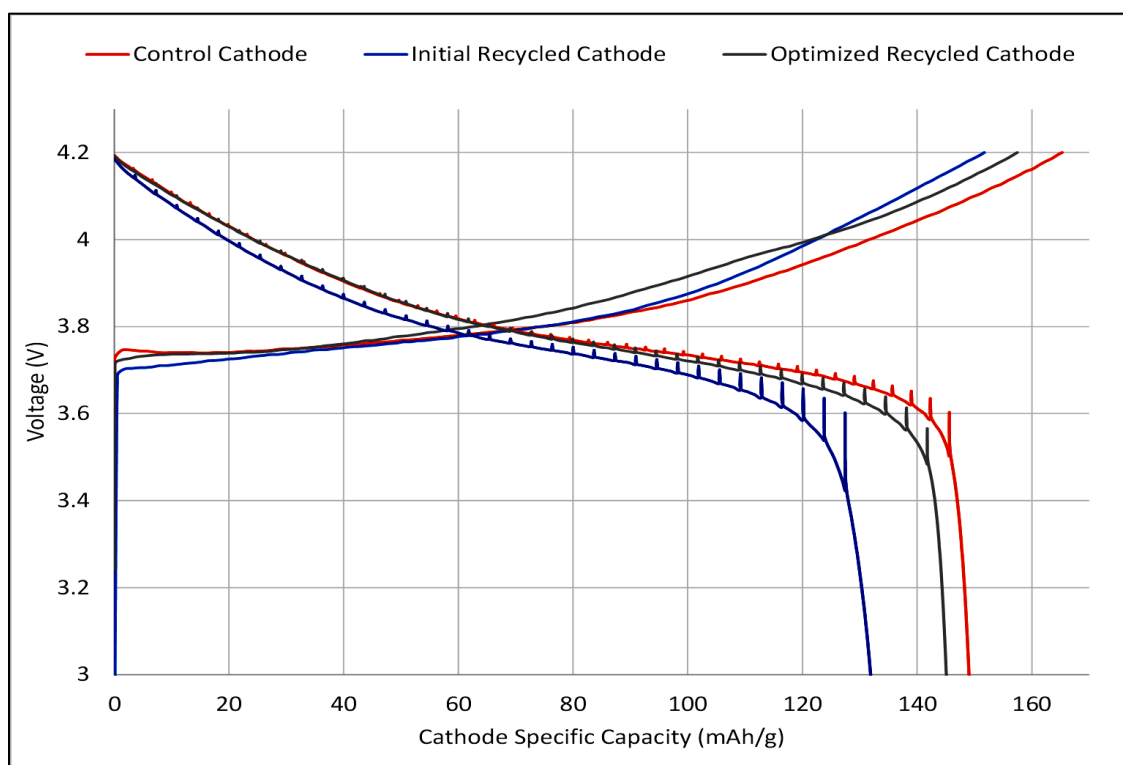
Coin cells were made and tested at Farasis, to determine the capacity (ability to hold lithium) of the recycled materials at certain points throughout the direct recycling process. A degradation of capacity might indicate that the recycling process parameters are chemically incompatible with the material. For example, Figure 8 shows a comparison of voltage curves for pristine and recycled anode electrodes.

Extensive development effort for this project focused on optimizing the process steps, testing the impact of the process step on materials, understanding any issues and adjusting the process conditions, sequence or other key parameter. This was an iterative process which began with a focus on pristine materials. After optimization of the process conditions, the research team began working with materials harvested from fresh cells that had not been cycled. Again after further optimization, the researchers further developed/optimized the process steps on electrodes/materials harvested from fresh cells that were not fully discharged prior to disassembly, purposefully leaving the active materials in a more reactive state. This is a key issue as the material might be expected to interact more negatively with the process steps, relative to fully discharged active materials in a more stable, less reactive state. In real world applications, researchers would expect at least some of the battery waste stream to include materials that cannot be fully discharged prior to recycling. The final iteration involved validating the process steps on active materials recovered from cells cycled to the end of life. The researchers clearly found that the condition or state of the anode and cathode materials going into the direct recycling process could have a significant impact on many key factors that can impact the feasibility of the approach, including yield, relative performance of the materials to pristine materials and also to critical morphological and surface characteristics that can have major impacts on using the materials to make new cells. To a large extent, the work under this project allowed us to identify and overcome these barriers by modifying or developing new process procedures and conditions.

Without going into full details, in general, the graphite anode materials were quite robust and were not adversely affected by the original processing steps, irrespective of their recovery state of charge or aging exposure with only slightly lower capacity relative to pristine graphite as illustrated in Figure 8.

The recycled NMC metal oxide cathode materials were more sensitive to the original process conditions depending on their condition going into the process, whether pristine, recovered from a cell, the state of charge at recovery and whether they were aged to the end of life. Thus a major aspect of the effort was developing new process technology that would be effective irrespective of the condition of the cathode materials. For example, cathode material from cells not greatly aged and fully discharged were relatively easily recoverable with the proposed process steps and regenerated to achieve performance similar to pristine materials. However, the researchers discovered that cathode materials harvested above a specific state of charge, or that had undergone very aggressive aging, behaved significantly differently during the separation and regeneration process steps. Figure 9 shows an example of the evolution of the progress in optimizing the recycling conditions to achieve pristine cathode material from aged Li-ion cells, in which the initial methods produced material with higher impedance and about 10 percent lower capacity.

Figure 9: Voltage Curves of Pristine and Recycled Cathode Materials



Source: Farasis Energy, Inc.

To overcome this critical barrier the research team had to develop significantly new process conditions, procedures and process sequences. By the end of the project as shown in Figure 9, they could handle any incoming cathode material in any reasonably expected condition from a practical waste stream to produce a new cathode material with no more than a 2 to 5 percent lower capacity than a pristine material. Materials that had undergone less abuse could be recovered and regenerated to achieve an almost pristine state. Cycle performance in coin cells was comparable between the recycled and pristine materials, but the nature of lower capacity in the recycled NMC cathode materials requires further investigation.

After developing and optimizing the recycling process conditions using laboratory prepared cells, the researchers began working with production cells that had been aged and could be used for a full life cycle demonstration or direct recycling.

3.3 Life-Cycle Demonstration of Recycled Li-ion Cells

While much of the direct recycling process development was conducted using either pristine materials or materials that had been harvested from recently-manufactured cells, one of the major goals of this project was to demonstrate that EV-type Li-ion cells that have reached their end of life could be taken through the optimized direct recycling process steps, and their active materials used to make new cells with performance comparable to cells made from pristine

active materials. End-of-life for EV batteries can be loosely defined as battery capacity dropping to about 80 percent of its initial capacity at beginning of life, and for current technology this can translate to 1,000 to 2,000 complete charge/discharge cycles.

Figure 10: 10Ah and 25Ah Lithium-ion Pouch Cells Manufactured by Farasis



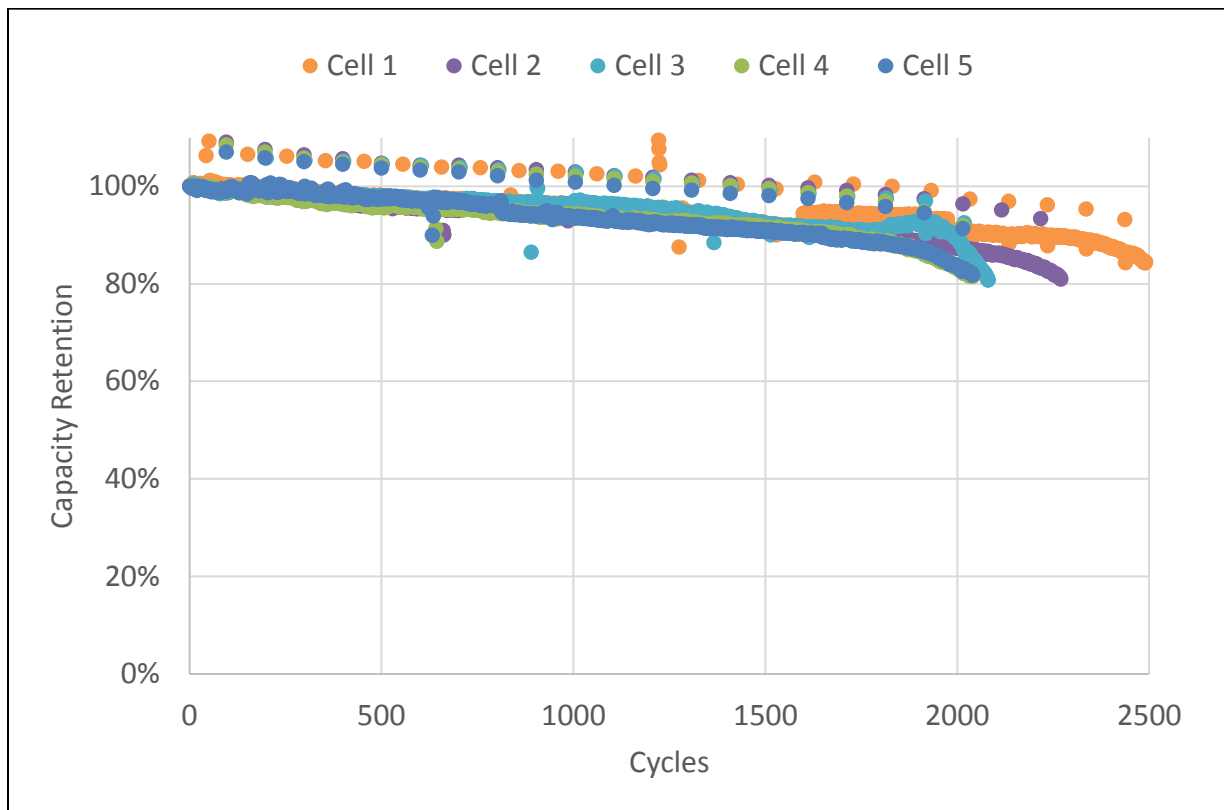
Photo Credit: Farasis Energy, Inc.

At the beginning of the project, cycle aging was initiated on several 10Ah and 27Ah Farasis Li-ion pouch cells (see Figure 10), two cell technologies that are currently being used in commercial electric motorcycle battery packs. Cells were cycled at a rate of 12 complete charge/discharge cycles per day, and thus the accelerated aging process achieved 2,000 cycles in approximately six months (see Figure 11). Cycling was performed in a controlled temperature environment at 30°C (86°F). The cells ranged in capacity retention over this period, from 89 to 78 percent.

For the purposes of life cycle demonstration at the lab scale, the cells were fully discharged before disassembly, both as a matter of safety and to preserve as much lithium in the cathode as possible. The cells were then disassembled by hand, and the anode and cathode electrodes were processed through the direct recycling purification and regeneration steps. The results of the purification and regeneration steps were quite promising, and returned yields upwards of 96 percent, one of the major goals for the project.

The purified and regenerated active material powders were mixed with binder, solvent, and conductive additives and coated onto new copper and aluminum foil current collector sheets to form new anode and cathode electrodes. A second cathode electrode was made using a mixture of 50 percent pristine active material and 50 percent recycled active material. Finally, a third cathode electrode was made using 100 percent pristine active material. The electrodes were all dried under vacuum, and assembled into new two-layer pouch cells, using the same (recycled) anode for all three cell types. In this manner, the impact of the direct recycling process on the cathode material, which showed greater susceptibility to processing conditions throughout the project, could be clearly demonstrated. The pouch cells had initial capacity of approximately 45mAh in this format.

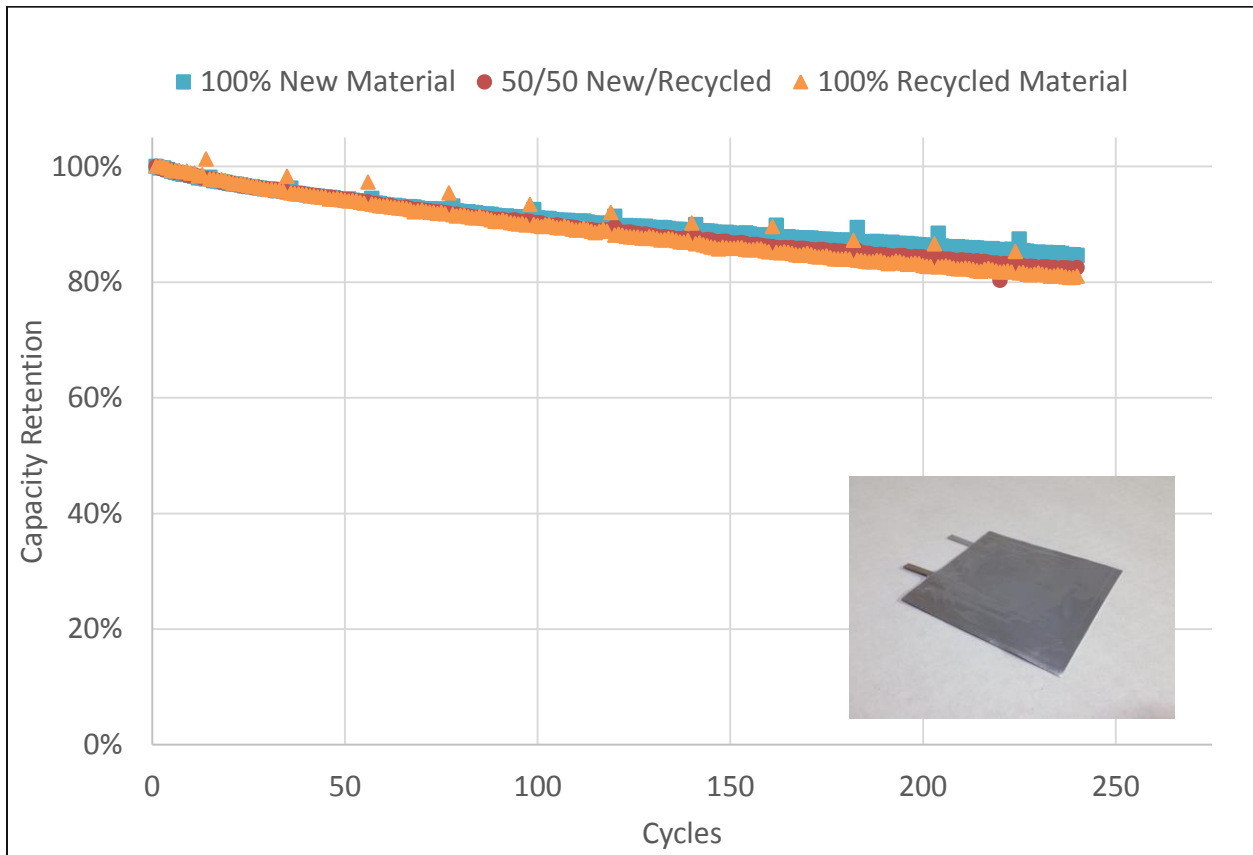
Figure 11: Cycle Performance Testing of Pouch Cells Used for Recycling Process



Source: Farasis Energy, Inc.

To complete the life cycle demonstration, cycle testing was initiated on the new cells to evaluate the performance of the Direct Recycled active materials. The initial capacities for the cells using 100 percent recycled cathode active material and the half new, half recycled material mixture were very similar to those of the control cells. Figure 12 shows the life cycle plots for the three cell designs. The cells were cycled at a rate of 4 charge/discharge cycles per day, and after 250 cycles the cells made using 100 percent recycled active materials had retained only slightly less capacity than the control cells.

Figure 12: Cycle Performance of Cells Made from Direct Recycled Materials



Source: Farasis Energy, Inc.

CHAPTER 4:

Conclusions and Recommendations

4.1 Conclusions

A major goal of this project was to develop, optimize, and scale-up several of the key steps in the direct recycling process. The impact of each process step on the pristine and harvested Li-ion battery material properties was evaluated to improve processing conditions and identify potential process/material incompatibilities. At the end of the project, a complete life cycle demonstration of the direct recycling technology was achieved. Lithium-ion cells that had been charged and discharged through more than 2,000 cycles were disassembled, and their electrode materials were ground, separated, purified, regenerated, and finally formed into new electrodes and cells. These cells were then subjected to life cycle testing, and after 250 cycles, capacity retention of cells using 100 percent recycled active materials was still within 5 percent that of control cells made using new materials.

The results of the life cycle demonstration, combined with materials testing and analysis performed throughout the project, indicate that the direct recycling process shows promise as a technology that is suitable to the NMC/graphite class of Li-ion batteries that proliferate in many of the EVs on the road today.

4.2 Recommendations

Several findings of this project warrant further research. While the recycled graphite materials generally showed resiliency to harvesting and re-use, recycled NMC cathodes materials consistently yielded about 5 percent lower capacity performance compared to the pristine material. Furthermore, the harvested cathode materials exhibited reduced particle size relative to pristine material, likely as a result of the initial cell manufacturing process. Such particle fracturing was not observed in earlier work related to harvested LCO cathode materials. The impact of such changes to the particle morphology on electrode performance should be investigated more thoroughly to better understand the long-term stability of recycled NMC cathode materials in the Li-ion cell environment.

4.3 Benefits to California

This project is an important step forward in establishing a sustainable Li-ion battery recycling industry for California's growing—and aging—fleet of electric vehicles. Direct recycling technology represents the most cost-effective and environmentally-friendly method for reclaiming and reusing the valuable components of spent Li-ion battery packs. Materials produced from direct recycling will be sold back to battery manufacturers and used to make new cells, providing a dependable revenue stream to support the recycling business, and helping to lower the cost of new cells. As the electric vehicle market continues to grow, direct recycling will provide the necessary solution to EV battery pack disposal, while minimizing the impact on California's landfills.

GLOSSARY

| Term | Definition |
|------------|-------------------------------------------------------------------------------------------------------|
| Ah | ampere-hour |
| anode | negative electrode of a cell |
| battery | a group of more than one cell connected together |
| black mass | ground mixture of anode and cathode powders from lithium-ion cells |
| cathode | positive electrode of a cell |
| cell | one unit of a battery, comprising alternating layers of anode and cathode with separator between them |
| cycle | charging a cell or battery, followed by discharging (or vise-versa) |
| EV | electric vehicle |
| g/cc | grams per cubic centimeter |
| kg | kilogram |
| LBNL | Lawrence Berkeley National Laboratory |
| LCO | lithium cobalt-oxide (LiCoO_2) |
| Li-ion | lithium ion |
| mAh | milli-ampere-hour |
| mL | milli-liter |
| NMC | lithium nickel-manganese-cobalt-oxide (LiNiMnCoO_2) |
| PEV | plug-in electric vehicle |
| R&D | research and development |
| SEM | scanning electron microscopy |
| TGA | thermogravimetric analysis |
| V | voltage, volts |
| Wh | watt-hour |
| XRD | X-ray diffraction |